CCXVIII.—The Explosion of Acetylene and Nitrogen. Part I.

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THE observations of Berthelot form the basis of almost every investigation into the phenomena of explosive processes, and it is thus not surprising that the reaction between acetylene and nitrogen was first studied by this great chemist. Berthelot showed that endothermic substances like acetylene, cyanogen, arsenic trihydride, and nitric oxide were readily detonated at atmospheric pressure by means of a fulminate detonator. The detonation could not, however, be brought about by an electric spark, in the case of acetylene, unless the pressure exceeded two atmospheres. A partial decomposition of the acetylene into carbon and hydrogen occurred during sparking, but the heat of decomposition was not liberated sufficiently quickly to start the explosion wave.

When acetylene and nitrogen are sparked at atmospheric pressure, carbon and hydrocvanic acid are produced (Berthelot, Compt. rend., 1868, 67, 1141). The decomposition of carbon can, however, be avoided and the conversion of acetylene into hydrocyanic acid made quantitative, in the presence of an excess of hydrogen, if the acid is removed by alkali as soon as it is formed. A further study of this reaction was made by Mixter (Amer. J. Sci., 1900, [iv], 9, 1; 1900, [iv], 10, 299), who exploded mixtures of acetylene and nitrogen in glass manometers and steel vessels. Both hydrocyanic acid and ammonia were found in the products of explosion. The primary reaction is probably the decomposition of acetylene into hydrogen and carbon, and this is followed by a reaction between the products and nitrogen. At the moment of explosion, among other substances, a mixture of carbon, hydrogen, and nitrogen is obtained, which reacts to give hydrocyanic acid and ammonia. The results of Wallis (Annalen, 1906, 345, 356) and Wartenberg (Zeitsch. anorg.

Chem., 1907, 52, 299) on the equilibrium between carbon, hydrogen, and nitrogen will thus be of interest. In these experiments with an equimolecular mixture of hydrogen and nitrogen it was found that about 40 per cent. of hydrocyanic acid was produced at 3300° and 4 per cent. at 1830° .

In many modern explosives, the deficiency of oxygen is so large that carbon is one of the products of detonation. During the cooling of the gases by radiation and by the work done on the container, this carbon reacts with the nitrogen present in the explosive to give hydrocyanic acid. The percentage of this gas in the gaseous products may be quite large, as was shown by Berthelot and Veille in the case of the detonation of benzenediazonium nitrate; 3.2 per cent. of the total gases was hydrocyanic acid. Trinitrotoluene also gives large quantities of hydrocyanic acid on detonation.

The products of an explosive decomposition are very largely determined by the rate of cooling; the slower the rate of cooling of the gases the lower the temperature at which the "chilling" of the gaseous equilibria takes place. This is of special importance in the hydrocyanic acid equilibria in the gases from explosives, for during the cooling a portion of the carbon liberated at the higher temperatures disappears according to the reaction:

$$\mathrm{CO}_2 + \mathrm{C} = 2\mathrm{CO}.$$

The presence of oxygen in the gases introduces a complication into the nitrogen equilibria, which makes their investigation difficult.

It was with the view of throwing light on these complex equilibria, occurring during cooling, that this investigation was undertaken. It was considered that the explosion of acetylene with nitrogen or of cyanogen with hydrogen would give rise to conditions which, while being similar to those occurring in the explosion of high explosives, would be free from the complications due to the presence of oxygen. The effect of the addition of oxygen to the mixture could then be studied.

EXPERIMENTAL.

(a) Materials.—The acetylene was obtained from a solution of this gas in acetone kindly supplied by Allen Liversidge, Ltd. Except for the presence of acetone, the gas was almost free from impurities; the first fraction gave 1-2 per cent. of hydrogen and nitrogen, but these constituents rapidly diminished to a negligible quantity as the acetylene was consumed. The percentage of acetylene in the gas liberated is calculated to be approximately 0.5 per cent. at a pressure in the cylinder of 20 atmospheres. It is

thus possible that the gas contained 0.25 per cent. of oxygen, and since the larger portion of this will be burnt to carbon monoxide, the amount of water produced on explosion will be very small. This small quantity of water formed on explosion, however, makes the analysis more difficult, for a mixture of hydrocyanic acid and ammonia in the presence of moisture attacks mercury.

The nitrogen was prepared from ammonium sulphate and sodium nitrite in aqueous solution in the presence of potassium dichromate (Veley, T., 1903, 83, 736); in addition, a little litharge was added. The nitrogen was stored over a suspension of ferrous hydroxide in water to remove nitric acid and to prevent the entrance of oxygen from the air, and was finally dried over phosphoric oxide. The mixtures of nitrogen and acetylene were analysed in a constantvolume apparatus.

(b) Bomb.—Preliminary experiments showed that dry hydrocyanic acid and ammonia were without action on the metals employed in the construction of pressure vessels, and there appeared to be no objection to the use of phosphor-bronze as a bomb material. A phosphor-bronze bomb, similar in design to that used by Wheeler (T., 1918, **113**, 855), but with 3/8 inch in thickness of walls and without the manometer, was obtained from Chas. Cook, the Manchester University Engineering Works. This was 3.988 litres in capacity and held a vacuum for twenty-four hours without appreciable leakage. A little vaselin was all that was necessary to make the joint gas-tight. It was found, however, that a loss of gas occurred at the large joint (annealed copper washer) at the moment of explosion, but as the joint held a vacuum after the experiment, this leakage was not a serious disadvantage.

(c) Measurement of Pressures.-Before the gas was introduced, the bomb was evacuated to a pressure of 1 mm. by means of a Cenco-Nelson oil-pump, and the pressure read off on a small McLeod gauge. The dry nitrogen was then introduced, and since the pressure did not reach 1 atmosphere, the measurement of this offered no difficulty. The acetylene was introduced directly into the bomb up to a pressure of 3.4 atmospheres, and after allowing time for the mixing of the gases, a sample was taken for analysis and the pressure measured accurately. For this purpose a new type of manometer was constructed, capable of reading up to five atmospheres. The principle adopted was to expand a known volume of the gas, at the pressure in the bomb, to approximately atmospheric pressure and to measure the new pressure on a mercuryglass manometer. A diagram of the manometer is given in Fig. 1. The apparatus consists of a series of glass bulbs A to B closed at both ends by two glass-to-metal taps A and B (J. Soc. Chem. Ind.,

1920, **39**, 247T) and attached to the manometer E. The volumes enclosed by mercury between the blue-glass tips a, b, c, and d and the tap A, were accurately determined.

Before the experiment, the apparatus is filled with mercury up to the tip a, and the tap B is closed. The gases from the bomb are then admitted into the first bulb, and the tap A is closed. Since in these experiments the pressure of the gas was 3-3.5 atmo-

FIG. 1. A E В

spheres, it was allowed to expand to the blue pointer, c, by opening the tap B and adjusting the level in E. The pressure was calculated from this level and the ratio of the volume of the bulbs. No correction was applied for the increase in volume in the first bulb, due to the compression of mercury and glass, since the order of accuracy required was less than 1 in 1000.

Explosion of Gases.

The explosive mixture was fired by the fusion of thin iron wire placed across the terminals in the centre of the bomb. Occasionally loss of gas occurred on explosion, which was detected by the smell of hydrocyanic acid. The joint, however, tightened up immediately and held a vacuum after the experiment. The bomb was distinctly warm to the hand after the explosion, and a

marked difference in the temperature of the thin metal parts was observed in experiments on the explosion of pure acetylene and that of a mixture containing 20 per cent. of nitrogen.

This behaviour would be explained by different rates of burning of the acetylene and nitrogen mixture. In experiment XIV, with 14 per cent. of nitrogen, it is evident that the explosion was incomplete.

Analysis and Measurement of Volume of Gases.

On account of the loss of gas (0.5 per cent.), the volume of the gases was measured after the explosion. The gases were led through bubblers (A, Fig. 2) to remove hydrocyanic acid and ammonia, into a large aspirator, F, fitted with a water manometer. The pressure in the aspirator was maintained at atmospheric, throughout, and the volume of the gases was measured by a determination of the water displaced. The first litre of gas, containing air from the bubblers, was measured and rejected. The remainder of the gas was collected in the aspirator and a portion analysed as a check. Some acetylene dissolved in the water, and the percentage of this gas was therefore low. For comparison, a sample was taken



directly from the bomb after the pressure had fallen to two atmospheres, and except for the slight difference due to the removal of a portion of acetylene in the first sample, the two analyses were in good agreement.

The gases in the bomb were dealt with in this way at pressures from three down to one atmosphere. From this point they were removed by means of a Toepler pump, B. On account of the small amount of water present, it was important to eliminate the hydrocyanic acid, ammonia, and water by means of liquid air, D, before passing the gases through the pump. The latter were collected at the base of the pump and transmitted through the bubblers, C, containing dilute acid and alkali, to the aspirator.

The total volume of the gases obtained in this manner, corrected for the vapour pressure of water and reduced to N.T.P., was used in calculating the percentages of ammonia and hydrocyanic acid.

The evacuation was carried out down to 2-3 mm., dry air admitted, and the bomb further evacuated. This was done as a

precaution, but the quantities of hydrocyanic acid removed at this stage were negligible.

The gases condensed in D were evaporated into the bubblers, A, and the solutions in C added to the respective solutions in A. The amounts trapped in C were negligible, showing that the whole of the hydrocyanic acid had been removed by liquid air.

The connecting tubes were all glass except where joined to the metal tube from the bomb by a short length of rubber tubing.

Hydrocyanic Acid and Ammonia.

It was found that hydrocyanic acid could be estimated by distillation from 0.5 per cent. sulphuric acid solutions without appreci-The gases could thus be absorbed in a series of able hydrolysis. bubblers, A, containing normal acid and dilute alkali. The acid solution containing hydrocyanic acid was then distilled into alkali and the whole of the hydrocyanic acid solutions were combined. The ammonia was estimated in the usual manner; the back-titration method gave the same result as the direct method. The hydrocvanic acid was estimated by (a) silver nitrate with potassium iodide as indicator (Denige, "Classen," Anal. Chem. p. 675), and (b) iodometrically (Fordos and Gélis, J. Pharm. Chim., 1853, [iii], 23, 48). The result obtained in (a) was usually 0.5 per cent. higher than that in (b); the mean value was taken.

The possibility of the loss of hydrocyanic acid by combination with the metal of the bomb must not be overlooked, but from the ease with which the results were reproduced (these are independent of the time the gases remain in the bomb) it appears that no appreciable action has occurred. Also, the interior of the bomb was as bright at the conclusion of these experiments as at the beginning. It was anticipated that the liquid hydrocyanic acid collected in the liquid-air tubes would show some tendency to polymerisation, but this was not found to be the case.

The carbon residue was analysed for hydrocyanic acid and ammonia, but these two gases were not present.

Permanent Gases.

The acetylene, hydrogen, and nitrogen in the residual gases were estimated in a constant-volume apparatus. Some difficulty was experienced in estimating the nitrogen with sufficient accuracy by the explosion method. In the later experiments, however, after the removal of the acetylene, the hydrogen was absorbed over copper oxide in a quartz tube, pure carbon dioxide being used to wash out the tube and to drive the gas into the measuring apparatus. The percentage of nitrogen was in good agreement with the calculated value (Table II). A little carbon monoxide could be detected in some of the experiments. Benzene and other condensed substances could only have been present in small amounts.

Discussion of Results.

The experimental data are given in Tables I and II, the Roman numerals indicating the order in which the experiments were performed. The results of all the experiments are given.

No. of expt.	Initial temp.	Initial per- centage of N.	Initial pressure in atm.	Final pressure in atm.	C.c. of HCN.	C.c. of \mathbf{NH}_3 .	Total volume of gases in c.c.
11	13°	2.97	3.21	3.02	(168.7)	(7.3)	12180
\mathbf{XIII}		3.15		3.24	203.6	14.2	12940
I	15	3.12	3.22	3.02	(123.0)	(4.0)	12180
III	14	3.29	3.24	3.10	(188.9)	(8.0)	12400
XI	16	5.29	3.24	$3 \cdot 27$	`282·8́	18.7	13090
VII	13.0	5.71	3.22	3.25	284.9	16.3	13000
v	10	9.66	3.26	3.16	340.1	16.8	
VIII	14	9.71	3.33	3.29	356.0	17.7	13240
VI	12	10.44	3.26	3.33	362.7	20.6	13310
IV	12.5	12.06	3.20	3.19	371.4		12750
IX	14	12.88		3.09	360.3	18.3	12370
XIV		14.27	******	3.24	360.3	$20.\bar{3}$	12950
x	15.5	18.04	3.26	3.10	381.0	20.5	12410
XĪĪ	18	22.05	3.01	2.95	388.2	16.9	12010

TABLE I.

The first three experiments I, II, and III may be disregarded, as in these cases the methods of analysis had not been completely worked out. With two exceptions the pressures of the mixed gases lie between 3.21 and 3.26 atmospheres. It will be observed that the volume of the hydrocyanic acid increases with the quantity of nitrogen in the gases, whereas the ammonia is almost constant throughout. The volume of gases given in the last column of Table I includes the hydrocyanic acid and ammonia.

The carbon deposited in the bomb was removed, mixed with copper oxide, and heated in a stream of carbon dioxide, and the amount of nitrogen present was determined. The volume of the nitrogen which was fixed on the surface of the carbon was certainly less than 1 c.c., that is, less than 0.01 per cent. of the total gas.

Since the main chemical reactions, during the explosion and the cooling of the gases, are not accompanied by any change in the number of molecules of gas, the initial and the final pressures should be the same. The values in the fourth and the fifth columns

TABLE II.

Percentage Composition of the Residual Gases.

No. of	N	9.	H	[
expt.	Calc.	Obs.	Calc.	Obs.	HCN.	NH3.	C_2H_2 .
п	2.25	(2.39)	93.6	(93.4)	1.38	0.060	2.76
XIII	2.28	`2·41´	$94 \cdot 1$	`94 ·0´	1.57	0.110	1.93
ĩ	2.63		$94 \cdot 2$		1.01	0.033	2.10
111	2.49	(2.77)	$93 \cdot 4$	(93.1)	1.52	0.062	2.34
XI	4.13	4·34	91.2	`91·0´	2.17	0.143	2.48
VII	4.55	(4.67)	91.3	(91.2)	2.19	0.122	1.78
v	8.25	(8.55)	86.3	(86.0)	2.69	0.133	2.63
VIII	8.28	(8-43)*	86.8	`86·7*	2.72	0.132	2.11
VI	9.00	(9.32)	85.8	(85.5)	2.73	0.154	2.29
iv	10.61	(10.81)	83.4	(83.7)	2.91		2.56
IX	11.34	(11.49)	83.5	(83·3)	2.92	0.148	2.12
XIV	12.80	`12·46´	78.7	`79·0´	2.78	0.121	5.53
X	16.42		78.1		3.01	0.165	2.24
XII	20.33	19.92	74.3	74.7	3.24	0.141	1.96

* Hydrogen estimated by the palladium method; the other values in brackets were obtained by the explosion method.

TABLE III.

No. of	N_2	[NH ₃]	$[NH_3]$	$[HCN]^2$	[HCN]
expt.	(Calc.)	[HCN]	[H ₂][HCN]	$[H_2][N_2]$	$[H_2][N_2]^{0.37}$
XIII	2.28	0.010	0.00074	0.0112	0.0126
XI	4.13	0.066	0.00072	0.0122	0.0141
VII	4.55	0.021	0.00063	0.0116	0.0132
v	8.25	0.049	0.00057	0.0101	0.0142
\mathbf{VIII}	8.28	0.020	0.00057	0.0103	0.0143
VI	9.00	0.021	0.00066	0.0091	0.0141
IV	10.61			0.0092	0.0142
IX	11.34	0.021	0.00061	0.0090	0.0143
XIV	12.80	0.057	0.00072	0.0077	0.0138
x	16.42	0.053	0.00068	0.0074	0.0140
XII	20.33	0.044	0.00059	0.0069	0.0143

(Table I) show the degree of correspondence between the initial and the final pressures measured at 0° . In general, the final pressures are somewhat lower, except in experiment VI, where it is possible that a leak of air inwards occurred during the measurement. The difference between the values is due, as previously mentioned, to the leak of gas at the moment of explosion.

In Table II is given the percentage composition of the residual gases. The nitrogen and hydrogen figures, columns 2 and 4, are obtained by difference, and these may be compared with the experimental figures in the next columns. The agreement is within experimental error. The explosion method of estimating hydrogen was not sufficiently accurate, many results being necessary to obtain the average value given in the tables; consistent results were obtained only by burning the hydrogen with oxygen over palladium or alone over copper oxide.

In order to arrive at the gas reaction constants in Table III, the calculated percentages of hydrogen and nitrogen have been employed.

In Fig. 3 the percentage of hydrocyanic acid is plotted against residual nitrogen. A smooth curve is obtained, which suggests a logarithmic relationship, possibly due to adsorption phenomena. The ammonia is almost constant throughout. The acetylene in the residual gases varies irregularly between 1.15 and 2.76 per cent.



(except in experiment XIV: 5.53 per cent.). As a small percentage of acetylene, in the neighbourhood of the walls and ignition plugs, must escape combustion, this irregularity is to be expected. In experiment XIV, however, explosion was less complete than usual. Similar percentages of acetylene are, however, frequently found in the gases from explosive processes, so that a portion of the acetylene in the above experiments is doubtless due to a combination of hydrogen and carbon at the high temperatures in the bomb.

Conclusions.

The chemical reactions which occur during the explosion of a mixture of acetylene and nitrogen are rendered fairly clear by

Wartenberg's theoretical analysis of the possible reactions (*loc. cit.*). Acetylene may decompose according to equation (1) or (2):

(1) $C_2H_2 = 2C + H_2 - 53000$ cals. (C amorphous).

(2) $C_2H_2 + N_2 = 2HCN - 2400$ cals.

The former is undoubtedly the principal reaction which occurs, for otherwise heat would not be liberated during the explosion. If this reaction goes to completion, and no dissociation of hydrogen occurs, it may be calculated that the temperature of explosion of pure acetylene is 3140° , whilst that of a mixture containing 10 per cent. of nitrogen is 3050° . In neither case can these temperatures be completely realised, for reaction (1) is reversible at high temperatures. This holds particularly for mixtures of nitrogen and acetylene, for not only can these substances react according to (2), but also the products of dissociation of acetylene will combine with nitrogen according to (3).

(3) $2C + H_2 + N_2 = 2HCN - 55400$ cals. (C amorphous). Both of these reactions take place with absorption of heat, so that the theoretical maximum of temperature is never reached.

At the temperature of explosion, therefore, the principal products will be carbon, hydrocyanic acid, acetylene, hydrogen, and nitrogen. During the process of cooling to room temperature, reaction (1) and the back reactions of (2) and (3) will take place, and the percentages of the gases in the cooled mixture will depend on the rate of cooling. The rate of cooling determines the "chilling interval" during which the chemical reactions are arrested, and we should expect the mixtures containing high percentages of nitrogen, on account of their slow rate of explosion, to be chilled at a lower temperature than nearly pure acetylene. It does not seem possible to decide between equations (2) and (3) from our results, though (3) gives a better constant. Wartenberg (Table IV) showed that the equilibrium constant of equation (3) decreased with decrease in temperature.

TABLE IV.

Temp.	K.		
2148° abs.	0.0092		
2025	0.0041		
1908	0.00157.		

It is found in our experiments that the relation $[HCN]^2/[H_2][N_2]$ varies from 0.0124 with 4.13 per cent. of nitrogen to 0.0069 with 20.33 per cent. of nitrogen. The former corresponds with the equilibrium constant at approximately 1950°, and the latter with that at 1800°, whence it appears that the reactants have been chilled at a lower temperature in the mixture containing 20 per cent. of nitrogen. The effect of rate of cooling on the equilibrium constant is, however, much greater than in the case of the watergas reaction (Andrew, T., 1914, **105**, 444), and the explanation of this perhaps lies in the nature of the heterogeneous reaction (3). The temperature coefficient of this reaction may be unusually large.

It is found that the empirical equation

 $\frac{[\text{HCN}]}{[\text{H}_2][\text{N}_2]^{0.37}} = \text{a constant} = 0.014$

holds over the range 4 to 20 per cent. of nitrogen. No explanation of this relationship can be given at present.

At lower temperatures, in the neighbourhood of 1300° and 1000° respectively, reactions (4) (Bergmann, J. Gasbeleucht., 1896, 117), and (5) may take place to an appreciable extent.

(4) $HCN + H_2 = C + NH_3 + 39800$ cals. (C amorphous).

(5) $N_2 + 3H_2 = 2NH_3 + 24100$ cals.

The calculations in Table III show that $[NH_3]/[H_2][HCN]$ is a constant within the experimental error of the ammonia estimation, indicating that hydrocyanic acid is the source of the ammonia.

Summary.

Mixtures of acetylene and nitrogen have been exploded at constant volume, and up to 3.24 per cent. of hydrocyanic acid has been found in the gases from the explosion. The results throw light upon the mode of production of hydrocyanic acid and ammonia in the cooling gases. The reaction constants for the equation

$$H_2 + N_2 + 2C = 2HCN$$

are found to vary between 0.0124 for 4.13 per cent., and 0.0069 for 20.33 per cent. of nitrogen in the residual gases, corresponding with a "chilling" temperature of 1950° and 1800° respectively.

The relation $\frac{[\text{HCN}]}{[\text{H}_2][\text{N}_2]^{0.37}} = 0.014$ has been found to hold for an

explosion of mixtures of nitrogen and hydrogen at 3 atm. pressure in a closed vessel of 4 litres capacity.

The concentration of ammonia bears a close relation to the concentration of hydrocyanic acid, and it is probable that this gas is produced according to the equation

$$HCN + H_2 = NH_3 + C.$$

A new type of manometer is described for the measurement of pressures up to five atmospheres.

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